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# Effect of liquid-phase sintering as a means of quality enhancement of pseudoalloys based on copper

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**Abstract.** The effects of the liquid phase of a metal binder on the microstructure and properties of self-diffusion gradient composite (Cu - Al - ZnO) were investigated. For the compositions considered, it was revealed that at the temperature of about 550 °C, a liquid phase binder forms from nanoparticles Cu - Al. Applying a proper amount of a (Cu - Al) binder appeared to be beneficial for fabricating gradient composites with the desired self-diffusion process. It is also favorable for mass transfer of additives nanoparticles into the volume of a matrix during sintering and for the desired fine microstructure and mechanical properties. For the experimental conditions considered in this study, the best mechanical properties can be obtained when 6 mass % (Cu - Al) of ligature were used, which gave hardness HB at 120, electroerosion wear – 0.092 • 10<sup>-6</sup> g / cycle, resistivity – 0.025 mΩm.

## 1. Introduction.

Analysis of accumulated information on basic physical - mechanical and exploitation properties of the electric contact materials shows that they are subjected to a variety of often conflicting requirements. Creation of electric contact materials, based on copper, and production of the articles that are based on them, requires the implementation of a variety of properties in one pseudoalloy: high enough (comparable to silver) electrical and thermal conductivity and, at the same time, the hardness, strength, wear resistance, corrosion and electrical discharge resistance. In order to provide the entire complex of numerous properties that define the reliable operation in a variety of conditions, age-hardening, refractory and anti-friction additives are introduced in the structure of the composite electrocontact material. This allows realizing the required complex of properties owing to efficient selection of phase components [1-3]. Previously, the authors and other researchers [4-7] showed that the implementation of the functional properties of the gradient to create materials for electrical purposes based on copper is not an alternative to the use of nanopowders. They can provide the required additional effect under the reduced amount of additives to the matrix material without reducing its own characteristics. It is well known that the use of conventional mixing and consolidation methods increases the initial size and agglomeration of nanoparticles and embrittlement of the matrix material. Therefore, for materials with elevated and uniform distribution properties of isolated nanoparticles, it is necessary to reduce their chemical interaction, agglomeration due to alternative techniques of preparing mixtures using intensive ultrasound preparation, for example, intensive plastic deformation, extrusion [8, 9]. The aim of this work is the development and justification of new technological methods and modes of introduction of ceramic ZnO nanoparticles in the structure of the electric contact materials based on

copper, which ensures their homogeneous, uniform distribution by volume and, as a result, improving physical and mechanical properties of pseudoalloys based on copper.

## 2. Result and Discussion.

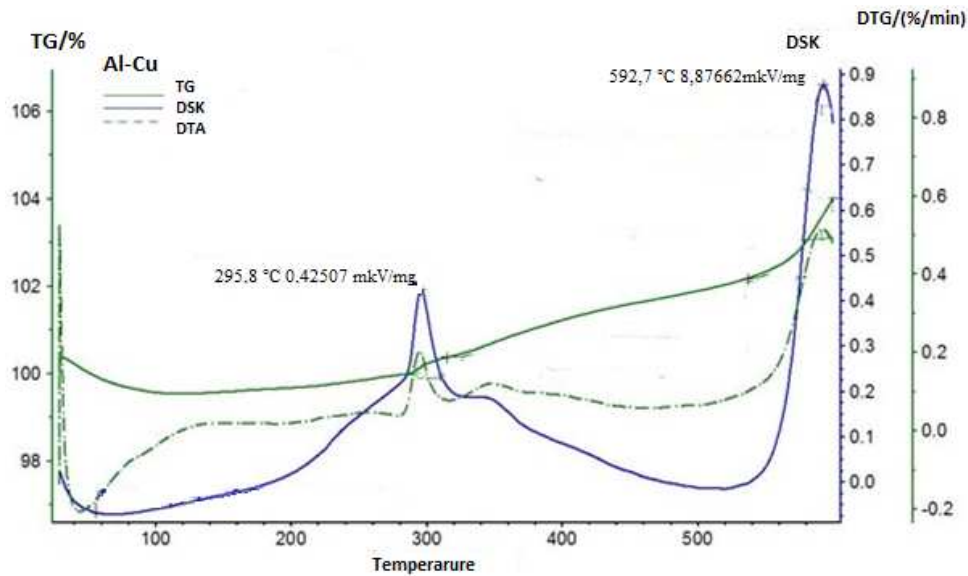
Plasticized powder mixtures based on copper with different chemical compositions and particle sizes were pressed into molds with a rigid matrix at a specific pressing pressure of  $P \leq 500$  MPa into tablets with dimensions  $\varnothing 10 \times 10$  mm, samples of electrical contacts KMK101020 (TU 16-685.020-85), control rods with dimensions  $5 \times 10 \times 50$  mm, plates with a thickness of 0.5 mm for conducting laboratory experimental studies of physical and mechanical properties and bench service tests.

Samples, sintered in several stages in vacuum, were further calibrated at pressure  $P = 800-1000$  MPa, and then annealed in vacuum at  $T = 500 \pm 20^\circ\text{C}$  to relieve residual stresses. Microstructures were studied by electron microscopy and energy dispersive microanalysis using the X-ray (CXR) by means of the microscope "JEOL JSM 6490LV, JEOL JSM 7001F" with the system microanalyzers "Oxford Instruments", "HITACHI TM 1000" and an optical microscope "ZEISS Observer Z1m". The intensity of the compaction process was assessed using the dilatometer "DIL 402", thermal analysis - using the derivatograph "Jupiter STA449C" and "SDT Q600 V20.5, X-ray analysis - using the diffractometer "D8 Advance". On the base of Divnogorsk Plant of low-voltage equipment (DZNV), electrical contacts were tested in terms of hardness, electrical resistivity, electroerosive wear (which was determined in accordance with ISO standards and sectoral methods).

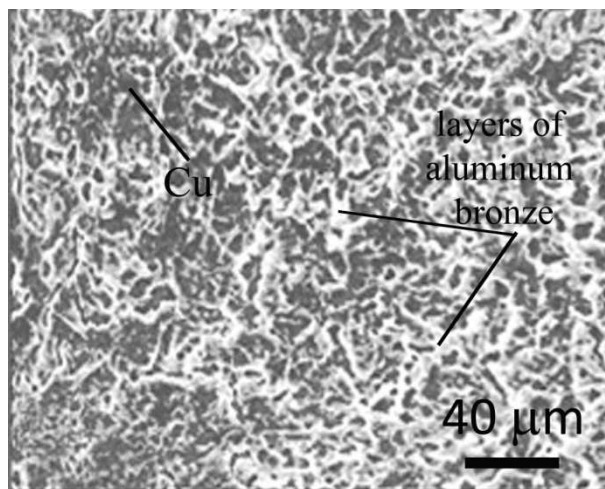
When setting objectives of experimental research, we proceeded primarily from the necessity to provide resistance to electric arc and to prevent weldability under the peak current loads (on - off). This can be achieved by using arc suppression additives of compounds (CdO, CuO, ZnO, WC, TiN), or owing to the use of high temperature metals (Mo, W). When defining the required amount of oxide phase ZnO in the structure of heterophase composite alloys by pre-calculated and experimental methods, numerical evaluation of the required concentrations of nanophase additives, including the use of stereological models for bimodal systems [5, 9]. An electron microscopic study of the microstructure, as well as the data of other investigators [5, 6, 8, 10] indicate that exceeding "threshold" concentration (about 8 mass %) leads to the formation of aggregates from nanoparticles and a framing grid along the grain boundaries. Such structural metamorphoses are unacceptable because of the substantial growth of the electrical resistance (120 microhm) and simultaneous embrittlement of matrix material, reduction of strength (1.5 - 2 times). To prevent formation of aggregates from nanoparticles and the framing grid, novel original methods of introducing nanoparticles to the material structure in the form of ligature are provided. For the production of electric contact materials, copper powder with an average particle size of  $d = 7$  mm; zinc oxide powder (obtained by shock-wave synthesis or by the method of chemical deposition from salts solution) and an average particle size of  $d = 8$  nm [5, 12], and composite powders of copper synthesized in a plasma arc discharge of low pressure [13] were used. The negative impact of the oxide phase on the electrical conductivity and heat conditions has been reduced by the introduction of the ZnO nano-powder into the basic mixture as ligature. The ligature contains the powders of copper and aluminum in a ratio of 94 wt % Al – 6 wt% Cu. Preliminarily, the model experimental tests were conducted with the use of ligatures (Al - Cu) using the nanosized of copper powders with the average particle sizes of  $d = 0.17$  mcm a specific surface area of  $S = 3.9 \text{ m}^2 / \text{g}$  and aluminum -  $d = 0.13$  mcm and the specific surface area of  $S = 16 \text{ m}^2 / \text{g}$ , obtained by the method of electrical explosion of wires [11].

Features of processes of structure formation of pseudoalloys, using ligature from the mixture of nanoparticles (Cu-Al), were studied by optical and scanning electron microscopy and thermal analysis (DTA, XRD, DSC, TGA – fig. 1, 2). At a temperature of about  $548^\circ\text{C}$ , the exothermic reaction starts with the formation of aluminum bronze from nanoparticles of copper and aluminum. Subsequently, the ligature was doped by additives of zinc oxide nanoparticles from the mixture of Cu and Al nanopowders. The quantity of ZnO nano additives in the ligature varied from 6 to 12% by weight. In turn, the content of the ligature made of Cu-Al-ZnO nanopowders in the composition of the basic matrix copper material amounts to 1-5 wt%. From the complex data, obtained by DTA, X-ray

diffraction and electron microscopy, it follows that the heat emission intensity (from 875 to 2250 J / g) is sufficient to form layers of aluminum bronze in local areas between the matrix grains of copper (Figure 3). Exothermic reactions of the thermoreactive synthesis are an additional source of activation energy. They provide a self-heating effect of ligature fraction (Cu-Al) in the volume of the powder workpiece during sintering. As a result of heat generation, the liquid layer of aluminum bronze is formed throughout the surface of matrix particles of copper. Along with "spreading", the liquid layer provides transportation of nanoparticles throughout the volume among the grains of copper and formation of the (heterogeneous) metal-ceramic structure of the pseudoalloy.

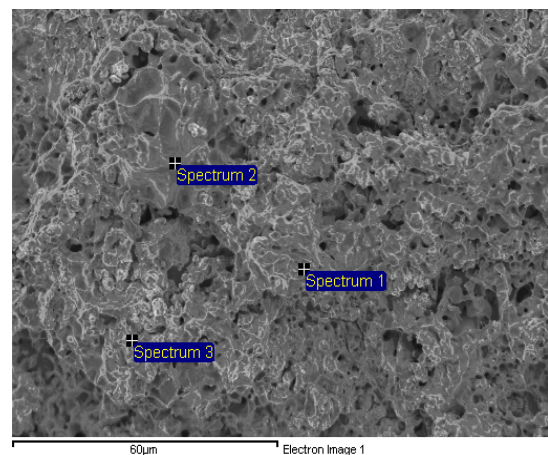


**Figure 1.** Results of thermal analysis of a mixture consisting of copper and aluminum nanopowders.



Copper and layers of aluminum bronze

a



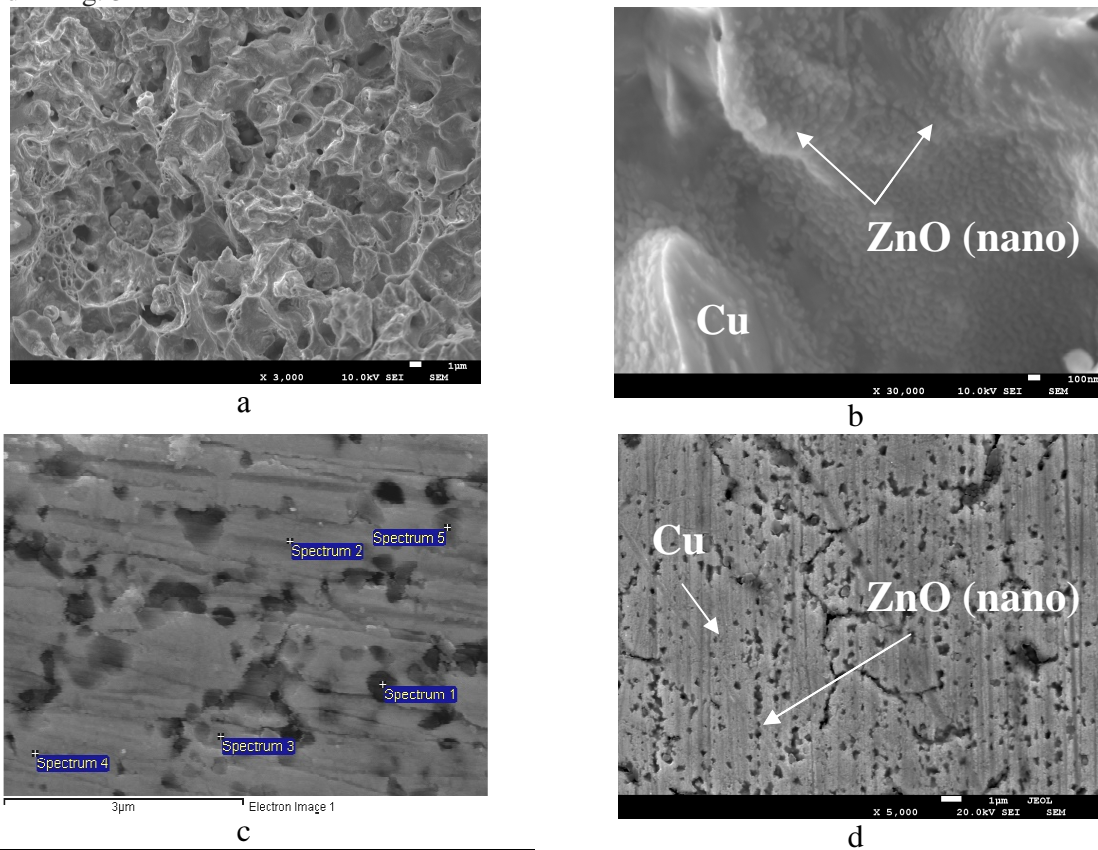
All results are given in wt%

Spectrum	Zn	O	Al	Cu	Total
Spectrum 1	1.98	2.72	2.33	92.97	100.00
Spectrum 2	1.52	0.54	0.59	97.35	100.00
Spectrum 3		1.52	1.51	96.97	100.00

b

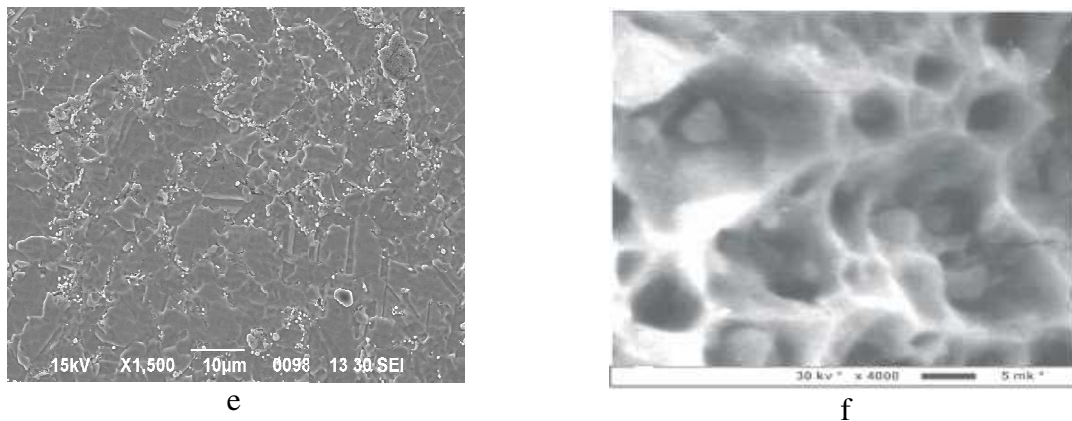
**Figure 2.** Formation of the pseudoalloy structure based on copper with the addition of nanoparticles ZnO nanoparticles: a - formation of layers of aluminum bronze; b – a general view of the additives of ZnO nanoparticles on the surface of the fracture

Later, the homogenization of the composite structure during sintering of the pseudoalloy (up to a temperature of about 920°C) allows redistributing the uniformly dispersed particles of ZnO throughout the volume of the copper matrix (Figure 2, 3). The results of DTA XRD, conducted at the same temperature (about 550 °C), subjected to phase transformation of aluminum up to its transition into a compound (Cu-Al), are confirmed. The nature of the nanoparticle additives distribution throughout the pseudoalloy volume is illustrated by electron microscopic analysis in Figure 3. Phase distribution and determination of the elemental composition are studied, using the method of energy dispersive microanalysis on the spectra of the characteristic X-ray (CXR), and using the method of compositional contrast. The results of determination of elemental composition in an atomic ratio are shown in Table 3c, and in Fig. 3



O, wt%	Zn, wt%	Cu, wt%	Total
12.12	29.67	58.21	100.00
	6.77	93.23	100.00
11.53	26.27	62.20	100.00
	2.17	97.83	100.00
5.14	15.12	79.74	100.00





**Figure 3.** Distribution of ZnO nanoparticles throughout the volume of the pseudoalloy based on copper: a, b - for fracture; c, d, e - on the surface; f - pits of ZnO additives on the fracture

The nanoparticles are distributed generally along the grain boundaries of the matrix material (copper), Figure 3f, as well as on the material within the grains. The observed phases larger aggregates are formed by ZnO nanoparticles with dimensions of 0.1-0.5 microns. However, partial agglomeration of nanoparticles does not reduce the overall required level of properties of electrical contact materials (comparable with the properties of standard grades of silver (Ag-CdO)).

Nanoparticles, statistically uniformly distributed due to the exothermic reaction throughout the volume of copper, contribute to the preservation of the fine-grained structure of the base material, and enable dispersion strengthening of the pseudoalloy (the hardness value increases up to 110 HB, compared with 60-70 HB in case of the matrix copper). An increase of the strength is confirmed by experimental data of microhardness measurements and by a decrease of the value of abrasive wear, Table 1 (along with providing arc suppression characteristics).

Thus, the realized method of obtainment of pseudoalloys Cu-ZnO (nano), namely, preliminary introduction of nanoadditives in the composition of the low-melt ligature made from nanopowders (Cu-Al-ZnO), provides a uniform distribution of ceramic additives (ZnO) throughout the volume of the mixture and in the structure of the final sintered material, and, as a result, the enhanced level of a complex of properties (table 1).

Operational testing of materials of contact pairs on the basis of the proposed method allowed us to determine optimum compositions of contact pair materials that provide an acceptable level of overheating in conditions of prolonged switching (more than 15 days) at 65 °C, commutation wear is within  $0.092 \cdot 10^{-6}$  g / cycle, specific resistivity of materials of the contact pair – 0.025 mcOm. Satisfactory arc blowing and opening of the contact pair in a short circuit are provided too (according to test results in the maximum switching capacity). Bench test results are presented in Table 1.

**Table 1.** The compositions and properties of the studied electric contact materials based on copper

Sample №	Material composition mass. %	Properties					
		Density $\gamma$ , g/sm <sup>3</sup>	Hardness HV	Electrical resistivity $\rho$ , mcOm	Electroerosion wear, $\epsilon$ , $10^{-6}$ , g/cycle	Temperature at the contact holder, °C	Strength limit, $\sigma$ , MPa
1	TiN 1.0 ZnO 2.5 (Cu – Al) ligature - 6 Cu matrix	8.6	110	0.022	0.310	73	2.0

2	TiN 2.5 ZnO 2.5 (Cu – Al) ligature - 6 Cu matrix	8.7	117	0.025	0.092	65	2.0
3	TiN 4.0 ZnO 2.5 (Cu – Al) ligature - 6 Cu matrix	8.6	120	0.027	0.340	78	1.8

The developed materials of the contact pair based on copper in their properties, can be recommended for replacement of standard contacts based on silver in the range of current loads up to 100 A (up to 500 A with short-term inclusion).

### 3. Conclusions

1. New data on the features of structure formation of composite pseudoalloys based on copper and modified by nanoparticles ZnO were obtained. Efficient technological methods of introduction of the nanoparticles in the copper-based material have been offered and proved. Introduction of nanoparticles into the structure of the material by using a liquid phase distribution throughout the ligature of aluminum bronze during sintering of contacts provide a uniform distribution of additives of nanoparticles of the ceramic phase in the volume of the matrix material (copper). The processing technologies have been suggested and justified to increase the distribution homogeneity of modifying nanoparticle additives ZnO over the volume of pseudoalloy, excluding their conglomeration

2. The optimum amounts of additives of modifying nanoparticles ZnO (up to 2.0% - 3.0% instead of 10-15% in comparison with known industrial trademarks) were determined. The main properties of the composite materials based on copper are resistivity  $\rho$  (about 0,025 mOm • m), strength of solder connection with the contact-holder material ( $\sigma \sim 2$  MPa). Electroerosion wear decreases (2.5 times in comparison with conventional materials) owing to dispersed inclusions of the ceramic phase.

### 4. Acknowledgements

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### REFERENCES

- [1] Gnesin G.G. 1981 *Sintered materials for electrical engineering and electronics. Reference edition.* (M, Metallurgiya) p. 344
- [2] Braunovic M., Konchits V. V., Myshkin N.K. 2007 *Electrical Contacts: Fundamentals, Applications, and Technology.* (London, New York: CRC Press, Teilorand Francis Gtoup) p. 646
- [3] Holm H. 2010 *Electric Contacts.* (Berlin; Springer-Verlang) p. 482
- [4] Shalunov E.P. 2007 Jarraud and wear-resistant copper granular composite materials with a mechanically reinforcing nanoparticles synthesized discs and high-resource products from them. *Nanotekhnika.* **1** 69-78
- [5] Nikolaeva N.S., Ivanov V.V., Shubin A.A., Sidorak A.V. 2013 The conductivity of the composite Ag / ZnO-based chemically precipitated mixtures. *Perspektivnye materialy* **8** 68-73
- [6] Gordeev Y.I., Zeer G.M., Zelenkova E.G., Abkaryan A.K., Surovtsev A.V., Teremov S.G., Plotnikov N.P. 2012 Prospects of Nanoparticles Application in Contact of Urban Electric Transport. *Russian Journal of Non-Ferrous Metals* **53** (4) 351-355
- [7] Andrievski R., Glazer A. 2009 Strength of nanostructures. *UFN* **179** (4) 337-358

- [8] Kolobov Yu.R., Valiev R.Z. 2001 *Grain Boundary Diffusion and properties of nanostructured materials* (Novosibirsk: Nauka) p. 232
- [9] Perel'man V. E. 1979 *Forming powder materials*
- [10] Gordeev Y.I., Adkaryan A.K., Binchurov A.V., Yasinsky V.B. 2014 Design and investigation of Hard Metal Composites Modified by Nanoparticles. *Advanced Material Research*. **1040** 13-18
- [11] Korshunov A.V. 2013 *Dimensional structural effects in the metal oxidation process: monograph*. (Tomsk.: TPU) p. 360
- [12] Beloshapko A.G., Bukaemskii A.A., Kuz'min I.G., Staver A.M. 1993 *Fizika goreniya i vzryva*. **29 (6)** 111-112
- [13] Ushakov A. V., Red'kin V. E., Zharkov S. M., Solov'ev L. A. 2003 The effect of pressure on the properties of the gas mixture of powders of titanium nitride electric. *Neorganicheskie materialy* **39 (3)** 337–341